

# Pilot-scale study on acid absorption process for ammonia removal from exhaust gas of denitrification catalyst

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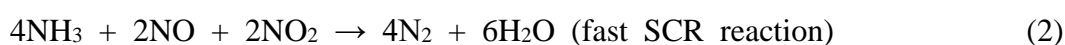
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**Abstract.** This paper presented the results of a study which aimed to removal ammonia from exhaust gas by sulfuric acid liquid. The results of the experiments indicated that absorption processes were efficient for removing ammonia from exhaust gas. pH 3.1 was high enough to removal ammonia from exhaust gas, and decreasing temperature of exhaust gas enhanced the removal efficiencies of NH<sub>3</sub>. In the case of pH < 3.0, the removal efficiency of NH<sub>3</sub> exceeds 95% over all conditions of reaction time.

**Keywords:** Ammonia emissions, ammonia absorption, sulfuric acid liquid.

## 1. Introduction

Removal of Nitrogen oxides (NO<sub>x</sub>) emissions from coal-fired power plants have always been the focus in coal's utilization industries for which it treated as a severe problem in the world through acid rain, photochemical smog. Furthermore, the spread of NO<sub>x</sub> into the atmosphere would destroy the atmospheric ozonosphere, disrupts the balance of radiation from the sun, leading to global warming and human beings through various health issues including skin cancer [1]. In the industrial field, the methods of exhaust gas recirculation (EGR) and selective catalytic reduction (SCR) technologies are commonly used to reduce NO<sub>x</sub> emissions [2]. The methods of EGR have its limits because it is difficult to meet the latest emission target requirements of the factory, therefore, many external purification treatment means are studied for many years, ammonia selective catalytic re-duction (NH<sub>3</sub>-SCR) technology is one of effective ways in denitration for converting NO<sub>x</sub> with the aid of a catalyst into N<sub>2</sub> and H<sub>2</sub>O, with the catalyst playing a key role in the process [3], and its main reaction process [4] is as follows:



Generally, SCR catalysts are synthesized by the reaction of titanium dioxide and ammonium heptamolybdate, in this process, some impurity gases released into emissions, such as ammonia, which may reach up to 20ppm. As a consequence, how to efficiently and economically remove the ammonia in flue gas is becoming a challenging task for environmental protection.

Many techniques, including biological filtration [5–7], liquid absorption [8–10], metallic compounds [11] and acid absorption [12] have been used to eliminate the NH<sub>3</sub> emission.

Biological filtration is being widely studied to treat NH<sub>3</sub> emissions, which has the characteristics of high removal efficiency and low operating cost. In spite of the potentials, biofilters efficiency decreases at inlet NH<sub>3</sub> loading rates above 20 gNm<sup>-3</sup>h<sup>-1</sup> of NH<sub>3</sub> depending on the design and operating conditions. Thus, NH<sub>3</sub> emissions above 30 gNm<sup>-3</sup>h<sup>-1</sup> usually need to combine the method of acid scrubbing in industrial facilities [13–14]. Ionic liquids (ILs), as a green solvent, can efficiently separate and removal NH<sub>3</sub> from industrial air stream containing ammonia, however, the relatively high viscosities of ILs and the limited gas-liquid interface severely affect its ammonia absorption efficiency, also the operation cost are relatively high due to high raw materials, which hinders their practical use in industries [15–16]. Metallic compounds such as magnesium chloride (MnCl<sub>2</sub>), Nickel

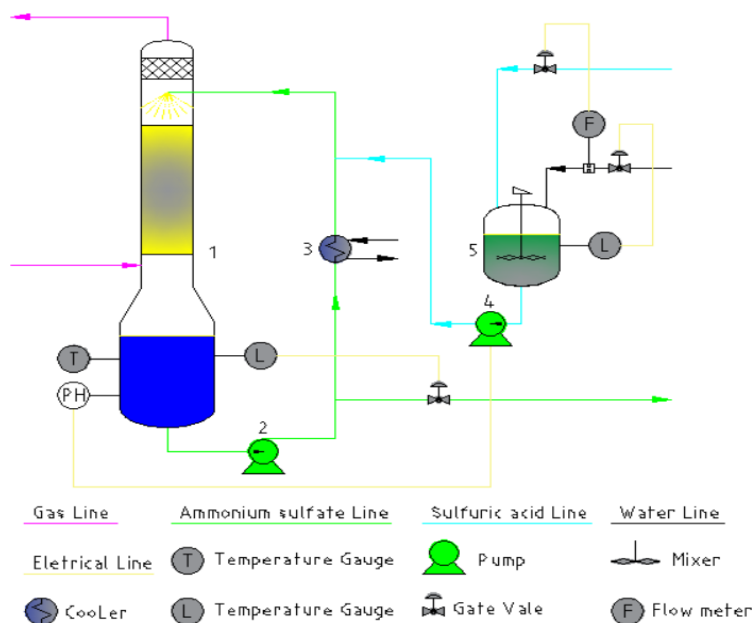
chloride ( $\text{NiCl}_2$ ) and other mixed metal halide, has been regarded as a promising effective control technology to separate ammonia at relatively low temperature and  $\text{NH}_3$  concentrations. Nevertheless, the limited adsorption capacity and stringent operating conditions reduces the applicability of metallic compounds in ammonia removal from the tail gas [17–18]. Among emission technologies for ammonia emission from exhaust gas mentioned above, acid absorption has been regarded as the greatest potential for removal technology, because of their higher absorption efficiency at low ammonia concentrations and high flow tail gas, furthermore, its viability for zero or less waste generation by recycling effluents as liquid fertilizer [19–21].

In this study, a sulfuric acid absorption system was designed to ammonia removal from exhaust gas of denitrification catalyst and concentrate for an improvement of economic feasibility, different gas temperatures and absorption fluid PH were studied to find the optimal operating conditions.

## 2. Experimental

The scheme of the pilot plant used in the experimental study is reported in Fig. 1. The plant consists of a continuously  $\text{NH}_3$  absorber scrubber, sulfuric acid storage tank, circulating pump, cooler and dosing pump. The  $\text{NH}_3$  absorber scrubber is a cylindrical tank constructed of reinforced polypropylene material (RPP) with an internal cavity for the pall ring that serves as increasing absorption area. The absorber scrubber capacity is approximately 141.0 m<sup>3</sup> with the following dimensions: 2.8 m inner diameter; 2.832 m outer diameter, 14 m media height and 1.500 m scrubber height. The bottom of scrubber is equipped with a thermowell containing a thermometer, liquid level meter, PH meter, and the temperature (55 °C) and PH (4.5) of the absorption liquid is respectively controlled by recycling cooling water flow and the content of sulfuric acid. Moreover, the control of optimal liquid level is provided by automatic system that control pumps and liquid level sensors.

As represented in Fig. 1, the scrubber is connected to a dilute sulfuric acid supply system, composed of a dilute sulfuric acid supply pump and a pot. More in detail, the water (W) was blended with dilute sulfuric acid (DSA) with certain blend ratios (W/DSA: 70/30, wt/wt) in the pot equipped with stirring. At the beginning of the operation, the bottom of the absorption scrubber is filled with 2.0 m sulfuric acid, and a dedicated pump provides continuous circulation of the liquid solution to the top of the scrubber (flowrate 20 m<sup>3</sup>/h). Thus, the process of reactive absorption occurs inside the packed column between the ammonia contained in the exhaust gas and the diluted sulfuric acid, producing ammonium sulphate. Concerning the exhaust gas discharged from the top of the packed column after ammonia removal, it is emitted to the atmosphere. During the process, the liquid solution is enriched in ammonium sulphate and depleted of sulfuric acid, and is accompanied by an increase in pH, in order to maintain the operating conditions of pilot plant experimentation, sulfuric acid is continuously added to the absorption solution to maintain a constant PH.



**Figure 1.** Process flow diagram (PFD) of the pilot plant. Numbers indicate the equipment units: 1 NH<sub>3</sub> absorber scrubber, 2 circulating pump, 3 cooler, 4 dilute sulfuric acid supply pump, 5 acid tank.

Input and output concentrations of NH<sub>3</sub> gas were analyzed by a portable emission and combustion gas analyzer (AR500, SMART SENSOR Ltd.). The removal efficiency of NH<sub>3</sub> gas was calculated as follows.

$$\eta_{NH_3} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (3)$$

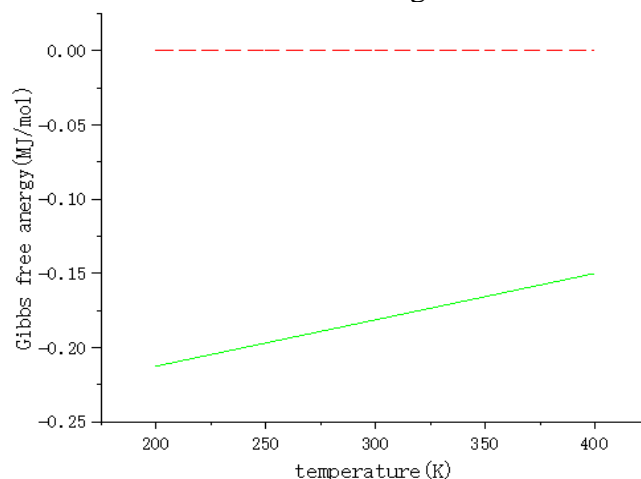
Here, C<sub>in</sub> and C<sub>out</sub> are the inlet and outlet concentrations of NH<sub>3</sub>.

### 3. Results and Discussion

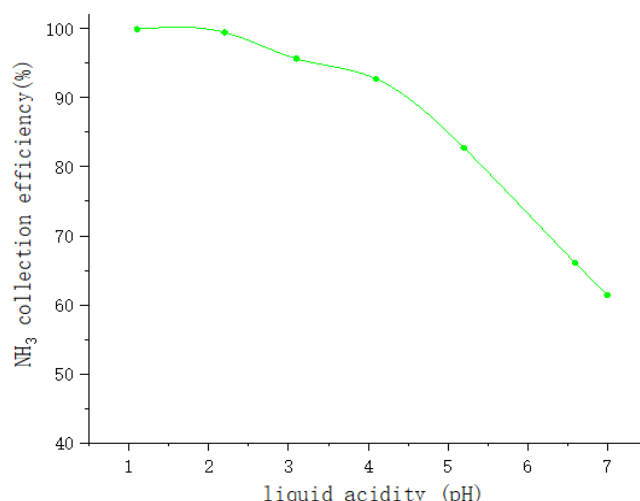
The chemical reaction between ammonia and sulfuric acid is as follows:



As shown in Figure 2, the standard Gibbs free energy changes ammonia and sulfuric acid is negative at the operating conditions. Therefore, it is expected that ammonia will spontaneously convert to ammonium sulfate in the chemical reaction region.

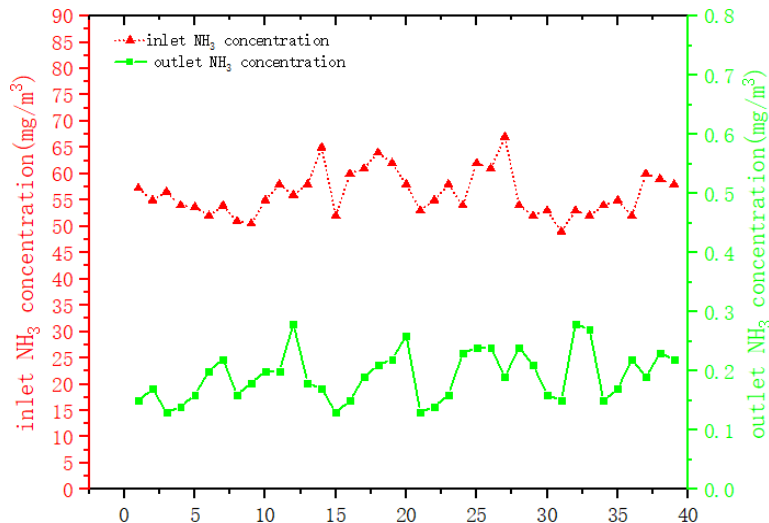


**Figure 2.** Standard Gibbs free energy changes for reactions between ammonia and sulfuric acid at different temperature



**Figure 3.** Effect of circulating liquid acidity (pH) on NH<sub>3</sub> collection efficiency

Figure 3 illustrates the effect of circulating liquid acidity (pH) on NH<sub>3</sub> collection efficiency for a constant inlet NH<sub>3</sub> concentration of 50 ~ 53 mg/m<sup>3</sup>. Results showed that liquid acidity had a significant effect on the absorption efficiency of the scrubber. Upon the circulating liquid acidity decrease from pH = 7.0 to pH = 4.1, the scrubber of NH<sub>3</sub> collection efficiency rapidly increased from by 61.40% to 92.72% (SE = 4%, p = 0.0004). As discussed by Hadlocon, et al (2015). At pH > 4.1 the solubility of NH<sub>3</sub> was further limited due to the evaporation of NH<sub>3</sub> in liquid back to gas phase. As is shown in figure 3, the increase of [H<sup>+</sup>] in liquid improved NH<sub>3</sub> collection efficiency, and the absorption efficiency started to level off and did not significantly change with acidity change.



**Figure 4.** Effect of circulating liquid acidity (pH) on NH<sub>3</sub> collection efficiency

Figure 4 shows the removal efficiencies of NH<sub>3</sub> remains constant as the reaction time. In the case of pH < 3.0, the removal efficiency of NH<sub>3</sub> exceeds 95% over all conditions of reaction time.

#### 4. Conclusion

This paper presented the results of a study which aimed to removal ammonia from exhaust gas by sulfuric acid liquid. The results of the experiments indicated that absorption processes were efficient for removing ammonia from exhaust gas. pH 3.1 was high enough to removal ammonia from exhaust gas, and decreasing temperature of exhaust gas enhanced the the removal efficiencies of NH<sub>3</sub>.

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